

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Catalyst and the Production thereof

We, CHEMETRON CORPORATION, of 840 North Michigan Avenue, Chicago 11, State of Illinois, United States of America, a corporation organized and existing under the laws of the State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a method of preparing a metal catalyst and to the catalyst produced thereby. More particularly it relates to the production of a nickel, cobalt or copper catalyst supported on an inert carrier in highly active, finely divided form suitable for use in the hydrogenation of an organic compound.

Metal catalysts, e.g., nickel catalysts, cobalt catalysts and copper catalysts, on inactive or inert carriers such as kieselguhr, diatomaceous earth and pumice have been made for many years. Although such catalysts, for example nickel catalysts, are generally active in the hydrogenation of organic compounds, particularly in the hydrogenation of double bonds in unsaturated fats and oils, they have numerous disadvantages such as relatively low activity, instability, high apparent density and complicated preparative procedures. It is important that the surface area of the metal on the support be as large as possible in order to prepare a highly active catalyst. Consequently, the steps used in preparing the catalyst affect the activity of the finished product and varying degrees of activity can be obtained by the use of different preparatory methods. The prior art methods which have been heretofore prescribed primarily for the preparation of the supported nickel catalysts have not produced catalysts of optimum activity characteristics. Simple impregnation of solid carriers with solutions of soluble nickel salts and subsequent reduction gives good catalysts but the nickel is not in as fine a condition as desirable for the best results.

When an insoluble nickel compound is precipitated in a slurry with the carrier, the carrier is not properly impregnated, and a major part of the nickel precipitate is merely in admixture with the carrier and only a small part of the precipitation occurs within the pores of the carrier. As a consequence the catalysts prepared by the calcining of the slurry of precipitated nickel salt and carrier are not as effective as might be desired.

It is an object of this invention to provide an improved supported metal, e.g. nickel, catalyst and a method of preparing the same. Another object of this invention is to provide an improved method for impregnating a porous carrier with catalytically active metals. A further object is to provide a supported metal catalyst which can be prepared economically and which has high activity per weight of active material.

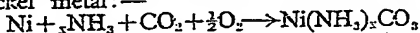
According to the present invention a method of preparing a supported metal catalyst, wherein said metal is selected from the group consisting of nickel, cobalt, copper, manganese, platinum, palladium, mercury, cadmium, gold and zinc, comprises forming an aqueous solution of metal ammine carbonate, the ammine carbonate containing at least 2 moles of ammonia per gram atom of metal, suspending an inert carrier in the resulting metal ammine carbonate solution, adjusting the relative ammonia and carbon dioxide contents of said solution to cause a basic metal carbonate to precipitate on the carrier, calcining the mixture of basic metal carbonate and carrier to form a metal oxide on the carrier, and at least partially reducing the metal oxide to metal supported on the carrier.

In the following disclosure particular reference is made to nickel for the purpose of exemplification.

Thus, we have found for example that a highly active, finely divided nickel catalyst

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on an inert support is produced by a series of operations commencing with nickel metal of high purity. Nickel metal or compound, preferably in finely divided form, is suspended in an aqueous solution of ammonia and carbon dioxide and treated with oxygen at a temperature of 50° F. to 140° F. to produce an aqueous solution of nickelammine carbonate of high purity, according to the following equation which is applicable to nickel metal:—



wherein x represents an integer of at least 2



The carrier with its coating of basic nickel carbonate is removed from the solution and is calcined, thereby decomposing the basic nickel carbonate to nickel oxide in the form of a finely divided particle layer on the entire surface of the carrier. The catalyst is then reduced with hydrogen or other reducing gas to form a mixture of elemental nickel and nickel oxide on the carrier. This reduced product is a highly active hydrogenation catalyst which is particularly desirable in the hardening of oils and fats.

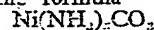
In the process generally described above, a number of critical features have been discovered. The nickel metal is used in preparing the nickel catalyst of this invention is preferably in finely divided form in order to accelerate its conversion nickelammine carbonate. In practice we prefer to use nickel powder in which 90% or more of the particles are finer than 200-mesh. Such nickel has a surface area of about 70 square centimeters per gram of metal. Other forms of nickel, such as nickel hydroxide and nickel oxide may also be used. When commercial nickel powders of finer than 100-mesh are used, 1100 to 1200 lbs. of nickel are required to produce a charge of 100 lbs. of nickelammine carbonate per hour with slow agitation and with air as the oxidizing medium. If oxygen is used as the oxidizing medium, only 400 to 500 lbs. of nickel powder are required to produce 100 lbs. of nickel in the form of nickelammine carbonate per hour. With high speed agitation the time required would be reduced to about 200 lbs. of nickel powder to produce 100 lbs. of nickel as nickelammine carbonate per hour.

The aqueous solution in which the nickel is dissolved should contain 6% to 10% ammonia by weight although higher concentrations of ammonia to about 15% are suitable. Above 15% the loss of ammonia is excessive in most applications. The aqueous solution should also contain 2% to 10% carbon dioxide by weight. With a solution containing 10% ammonia and 4% carbon dioxide, nickel concentrations up to 2% are readily obtained. The resulting nickel-

and preferably has the assigned value of 6. The nickelammine carbonate solution is then separated from any undissolved nickel powder and is heated to cause evaporation of the ammonia and carbon dioxide. The heating is done with agitation in the presence of a solid carrier, such as kieselguhr, and as the ammonia evaporates basic nickel carbonate in finely divided form, uncontaminated with other metal salts, is produced and precipitates on the inert carrier forming a large-surface layer of finely divided basic nickel carbonate. The reaction may be represented as

ammine carbonate solution may be diluted or otherwise brought to the desired nickel concentration prior to heating to evaporate part of the ammonia in the presence of the slurry of carrier. The concentration of the nickel in the solution should be in the range of 0.1% to 5% by weight and preferably about 1%. It is preferable for the solution to contain at least one mole of available carbon dioxide per gram atom of nickel. The amount of carrier, such as kieselguhr, which is added to the nickelammine carbonate solution, should vary from 1/10th to 10 times the weight of the nickel in such solution and generally amounts to 8 to 45 grams of carrier per gallon of nickelammine carbonate solution.

The precipitation of the basic nickel carbonate on the support ordinarily conducted at a temperature in the range of 203° F. to 212° F. at a pressure of 1 atmosphere. If reduced pressure is used, the precipitation can be conducted at lower temperatures in the range of 180° F. to 203° F. The heating is preferably done by live steam which drives off some of the excess ammonia, thereby slightly lowering the pH and destroying the nickelammine complex, thereby causing basic nickel carbonate to precipitate in and on the carrier. The nickelammine carbonate complex has the formula



wherein x may be an integer in the order of even numbers from 2 to 6. As the value of x is reduced by evaporation of the ammonia, a basic nickel carbonate is formed which is insoluble in the aqueous phase. The precipitate of basic nickel carbonate on the inert carrier, such as kieselguhr, can be removed by filtration and no washing is needed in order to prepare a satisfactory catalyst; the nickel salt is of high purity with respect to metal. The precipitate of basic nickel carbonate and carrier is deep green in color and should preferably contain at least 2.0% carbon dioxide in catalysts wherein the nickel to carrier ratio is 1:1 for ease of reduction after calcination. The higher the carbonate content of the basic nickel carbonate on the carrier, the more readily the catalyst is reduced. The

filter cake is dried at a temperature up to 250° F. and then calcined at 650° F. to 850° F. or it may be directly calcined at 250° F. to 850° F. During the calcination step the basic nickel carbonate is decomposed to nickel oxide. The density of the catalyst after calcination varies from 0.116 to 0.338 grams per cubic centimeter. The density generally depends upon the ratio of nickel to support, higher nickel content resulting in higher density. After calcination the catalyst is treated with hydrogen gas or other reducing medium, preferably at a temperature in excess of 700° F., to reduce part of the supported nickel oxide to nickel metal. In the final catalyst approximately half of the nickel is in a form of nickel oxide and generally the amount of nickel oxide runs from 30% to 80% of the total nickel in the catalyst. The percent reduction varies linearly with increase in temperature. The percentage reduction at a given time and temperature increases linearly with increasing ratio of nickel to support. The optimum amount of reduction appears to be in the neighbourhood of 60% giving a catalyst of high initial activity and maximum reuse.

The ratio of nickel to support appears to have an effect on the amount of nickel reduced at a given time and temperature. Higher nickel ratios make the catalyst more readily reduced; increasing the nickel-to-support ratio from 1:1 to 2:1 almost doubles the percent reduction in a given time at a given temperature. Good catalysts having initial activity of 16–20 minutes in the test procedure subsequently described and 20 to 25 reuses can be made on methods of this invention wherein 44% to 55% reduction of the nickel oxide or nickel is optimally attained at a temperature of 700° F. to 800° F.

The catalyst is highly active and must be covered with oil or otherwise protected from the atmosphere to prevent reaction with oxygen, or it may be stabilized by treatment with a stream of carbon dioxide gas containing controlled quantities of oxygen. Reduction of the nickel oxide on the carrier takes place to a greater extent at lower temperatures when the nickel-carrier ratio is high. For instance, a catalyst of good initial activity is produced even when only about 20% of the nickel oxide is reduced to nickel when the catalyst contains one part of nickel to one part of kieselguhr. Generally, not more than 50% reduction of the nickel oxide to nickel metal is required in a catalyst containing equal parts of nickel and carrier. The reduction is ordinarily carried out at relatively high temperatures in the range of 500° F. to 1000° F. for 3 to 12 hours.

While the invention has been described with reference to nickel by way of example, it is also applicable to cobalt, copper, man-

ganese, platinum, palladium, mercury, cadmium, gold and zinc, and catalyst containing these metals can be produced in the same way. The invention is adaptable to the production of composite catalysts containing two or more metals of the group consisting of nickel, cobalt, copper and zinc. For instance, a nickel-cobalt catalyst on kieselguhr can be produced by evaporating ammonia and carbon dioxide from a solution of nickelamine carbonate and cobaltamine carbonate having kieselguhr suspended therein, and subsequently calcining and reducing the precipitate.

The following examples illustrate the preparation of catalysts within the scope of this invention and the use of such catalysts in the hydrogenation of fats and oils.

EXAMPLE 1

500 parts of nickel powder (99.9% nickel) in 2000 parts of water containing 76 parts of ammonium carbonate monohydrate and 97.5 parts of 29% aqueous ammonia were mixed in a leach vessel and agitated while air was bubbled into the bottom of the tank through a fritted sparger. The solution was heated to 90–100° F. by external heat and the reaction 110° F. In about two hours a blue nickel-amine carbonate solution was formed containing about 3.6% nickel.

The nickelamine carbonate solution was decanted from undissolved nickel and diluted with water to a concentration of 7.6 grams of nickel per gallon. Then an amount of kieselguhr equal to the weight of nickel in the nickelamine carbonate solution was added and live steam was blown into the bottom of the kettle to provide heat and agitation. The temperature of the suspension was allowed to rise to 204° to 210° F. in approximately three-quarters of an hour. The mixture was held at boiling temperature until the supernatant liquid, when observed in a 250 ml. beaker, was just slightly blue, indicating that substantially all of the nickel had precipitated as basic nickel carbonate. The green precipitate was removed by filtration while hot, and the filter cake of basic nickel carbonate on kieselguhr was dried at 110° C. The dried filter cake was immediately calcined at 650° F. to form nickel oxide on the kieselguhr carrier. The density of the nickel oxide on kieselguhr product after calcination was 0.214 gram per cubic centimeter. The catalyst was reduced in a stream of hydrogen for 3 hours at 700° F., resulting in a catalyst in which 35.6% of the nickel oxide was reduced to nickel metal and having a high activity as a hydrogenation catalyst.

EXAMPLE 2

390 parts of ammonium carbonate monohydrate dissolved in 1030 parts of 29% aqueous ammonia and 847 parts of water provided a solution containing 13.9%

ammonia and 5.0% carbon dioxide. A suspension of 4 parts of nickel powder (90% finer than 100-mesh) in 200 parts of the foregoing solution was agitated while a stream of air was bubbled into the bottom of the vessel through a sparger. After one-half hour the nickelammine carbonate solution, containing 21 grams of nickel per gallon, was removed by decantation and mixed with 4 parts of finely divided kieselguhr. The suspension was agitated and heated to about 200° F. with live steam during a period of one-half hour and held at 202–204° F. until all the nickel has precipitated (about 2 hours). The green precipitate of basic nickel carbonate and kieselguhr was collected on a filter and dried at 110° C. It was then calcined at 650° F. and produced a product of nickel oxide on kieselguhr having a density of 0.19 gram per cubic centimeter. This product was reduced at 1000° F. for 3 hours in a hydrogen stream and produced a catalyst in which 59.3% of the nickel oxide was reduced to nickel. This catalyst has an initial activity of about 26 minutes as a hydrogenation catalyst in the test procedure described below.

EXAMPLE 3

In a stainless steel kettle 34.5 litres of nickelammine carbonate solution containing 1.2% nickel were added to 25 liters of water. Then 400 grams of finely divided kieselguhr were added and the mixture agitated with live steam blown into the bottom of the kettle through a one-quarter inch stainless steel tube. The mixture was heated to a temperature in the range of 204–210° F. at approximately three-quarters of an hour. The mixture was held at boiling temperature until a filtrate was just slightly blue, indicating almost complete precipitation of the nickel. The precipitate was filtered while hot and the entire position was completed in about two to three hours. If temperatures are held too long near boiling point, there will be an excessive loss of carbon dioxide and the basic carbonate of nickel will be low in carbonate content.

The precipitate of basic nickel carbonate and kieselguhr was calcined at 750° F. and then reduced at 700° F. for 3 hours. The nickel oxide in the resulting catalyst was reduced approximately 22% to nickel. The catalyst so produced had an activity of 18 minutes by the test procedure given below.

TEST PROCEDURE

The activity of nickel hydrogenation catalyst produced in accordance with this application was measured by a procedure wherein a catalyst containing a given amount of nickel was used to hydrogenate the unsaturates present in cottonseed oil under specified conditions to reduce the refractive index thereof a specified amount. The drop in refractive

index corresponds to a reduction in the iodine value of the unsaturated oil from approximately 105 to 63. The length of time required for a given catalyst to produce the required drop in refractive index is inversely proportional to the activity of the catalyst.

The following procedure was used: A charge of 190 to 210 grams of cottonseed oil was placed in a cylindrical glass reactor fitted with a stainless steel paddle stirrer operating at a constant speed of 3600 rpm. Hydrogen at the rate of 700 to 800 cc. per minute was passed into the apparatus while the cottonseed oil was agitated and heated with an external electric heater. An amount of nickel catalyst was accurately weighed out equivalent to 0.05% of the weight of the cottonseed oil, based on the nickel content of the catalyst. For instance, if 200 grams of cottonseed oil were the charge, then an amount of catalyst containing 0.100 gram of nickel would be selected. When the temperature of the cottonseed oil reached 292–298° F. a 5 cc. sample was removed and its refractive index measured at 48° C. Then the catalyst was added to the oil and timing was started immediately. After about 12 minutes a further sample of cottonseed oil was removed and its refractive index measured after filtration to remove any catalyst. Further samples were removed from time to time and measured for refractive index so that the time when the refractive index had dropped 0.0051 from its original value can be measured. This time was taken as the measure of the activity of the catalyst. The smaller the time value in this test, the greater the catalyst activity in the hardening of vegetable oils. Generally, catalysts made according to this application have initial activities of 15 to 50 minutes.

WHAT WE CLAIM IS:—

1. A method of preparing a supported metal catalyst, wherein said metal is selected from the group consisting of nickel, cobalt, copper, manganese, platinum, palladium, mercury, cadmium, gold and zinc, which comprises forming an aqueous solution of metal ammine carbonate, the ammine carbonate containing at least 2 moles of ammonia per gram atoms of metal, suspending an inert carrier in the resulting metal ammine carbonate solution, adjusting the relative ammonia and carbon dioxide contents of said solution to cause a basic metal carbonate to precipitate on the carrier, calcining the mixture of basic metal carbonate and carrier to form a metal oxide on the carrier, and at least partially reducing the metal oxide to metal supported on the carrier.

2. A method of preparing a supported nickel catalyst which comprises forming an aqueous solution of nickel ammine carbonate, the ammine carbonate containing from 2 to 6 moles of ammonia per gram atom of nickel, suspending an inert carrier in the

- resulting solution of nickel-ammine carbonate evaporating ammonia from said solution to cause basic nickel carbonate to precipitate on the carrier, calcining the mixture of basic nickel carbonate and carrier to form nickel oxide on the carrier, and partially reducing the nickel oxide to nickel supported on the carrier.
- 5 3. The method defined in Claim 2 wherein the nickel ammine carbonate solution contains at least one mole of available carbon dioxide per gram atom of nickel.
- 10 4. The method defined in Claim 3 wherein the nickelammine carbonate solution contains 0.1% to 10% nickel.
- 15 5. The method defined in Claim 4 wherein the ammonia is evaporated from the nickel-ammine carbonate solution at a temperature in the range of 200° F. to 212° F.
- 20 6. The method defined in Claim 5 wherein the mixture of basic nickel carbonate and carrier is calcined at a temperature in the range of 650° F. to 850° F.
7. The method defined in Claim 6 wherein the calcined product is reduced at a temperature in excess of 600° F.
- 25 8. The method defined in Claim 7 wherein nickel metal is dissolved in an aqueous solution containing 6 to 15% ammonia by weight and 2 to 10% carbon dioxide by weight in contact with an oxygen-containing gas, the solution is separated from insoluble materials, and kieselguhr is suspended in the solution in an amount substantially equal to the weight of nickel present to form a nickel-nickel oxide catalyst on kieselguhr.
- 30 9. The method defined in Claim 8 wherein the oxygen-containing gas is air.
- 35 10. A method of preparing a supported nickel catalyst substantially as described in any of the examples.
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